



Stable p-block metals electronic perturbation in PtM@CNT (M=Ga, In, Pb and Bi) for acidic seawater hydrogen production at commercial current densities

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ARTICLE INFO

Keywords:

Alloy
Electronic regulation
Seawater
HER
Electrocatalyst

ABSTRACT

Achieving acidic seawater hydrogen production under commercial current densities remains a challenge. We present here a novel strategy through strong metal-support interaction (SMSI) and Pt-p-block alloys (PtM@CNT, M = Ga, In, Pb, and Bi) to construct a stable electronic perturbation and achieve acidic seawater hydrogen evolution performance at commercial current densities for the first time. SMSI stabilizes electronic perturbation and promotes durability up to 360 h. The optimized Pt₆₁Ga₃₉@CNT exhibits an overpotential of 18 mV at 10 mA cm⁻² in 0.5 M H₂SO₄ and maintains 360 h stability at 500 mA cm⁻² in acidic seawater. Density functional theory (DFT) calculation reveals that the optimized d-band center of Pt and ΔG_{H*} increase the catalytic activity, and the higher vacancy formation energy enhances the durability. Overall, this discovery not only first achieves stable acidic seawater hydrogen production under commercial current densities, but also opens a new opportunity to explore catalytic applications of p-block alloys and SMSI stabilized electronic perturbation.

1. Introduction

In response to global climate change and the rapid consumption of fossil fuels, the concept of hydrogen economy was proposed as a vision of the future economic structure [1,2]. As the popularity of renewable electricity, combining renewable electricity with electrochemical processes to produce hydrogen has attracted a lot of interest from academia and industry [3–7]. The arid coastal area is the preferred place to produce electrolytic hydrogen using renewable power, possesses sufficient photovoltaic and wind power potentials [8–11]. However, a large supply of freshwater will limit the electrolytic water technology for wider applications. Acidic electrolytes exhibit higher hydrogen evolution reaction (HER) kinetics due to the high concentrations of protons/hydronium ions [12,13]. Developing hydrogen production technology with acidic seawater as the electrolyte may solve the

problem of fresh water shortage and increase production capacity. Because of corrosive ions and acidic media, long-term stability under commercial current densities acidic seawater HER has not been realized [14,15]. Therefore, it is necessary to develop stable catalysts for acidic seawater hydrogen evolution at commercial current densities.

So far, platinum (Pt) plays an irreplaceable role in acidic HER [16, 17]. However, its high price, scarcity and poor stability severely restrict the practical application. Pt has a strong H adsorption activity, so its electronic structure should be adjusted to reduce the binding energy [18–20]. Many feasible strategies have been used to modulate the electronic structure of Pt including alloying [21], coordination regulation [22], crystal adjustment [23], strain engineering [24], etc. Among them, alloying strategy can not only adjust the electronic structure of Pt but also reduce the loading. Alloying Pt with 3d transition metals (such as Fe, Co, Ni) has been widely explored at present [25–27].

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<https://doi.org/10.1016/j.apcatb.2022.122100>

Received 21 May 2022; Received in revised form 28 September 2022; Accepted 23 October 2022

Available online 26 October 2022

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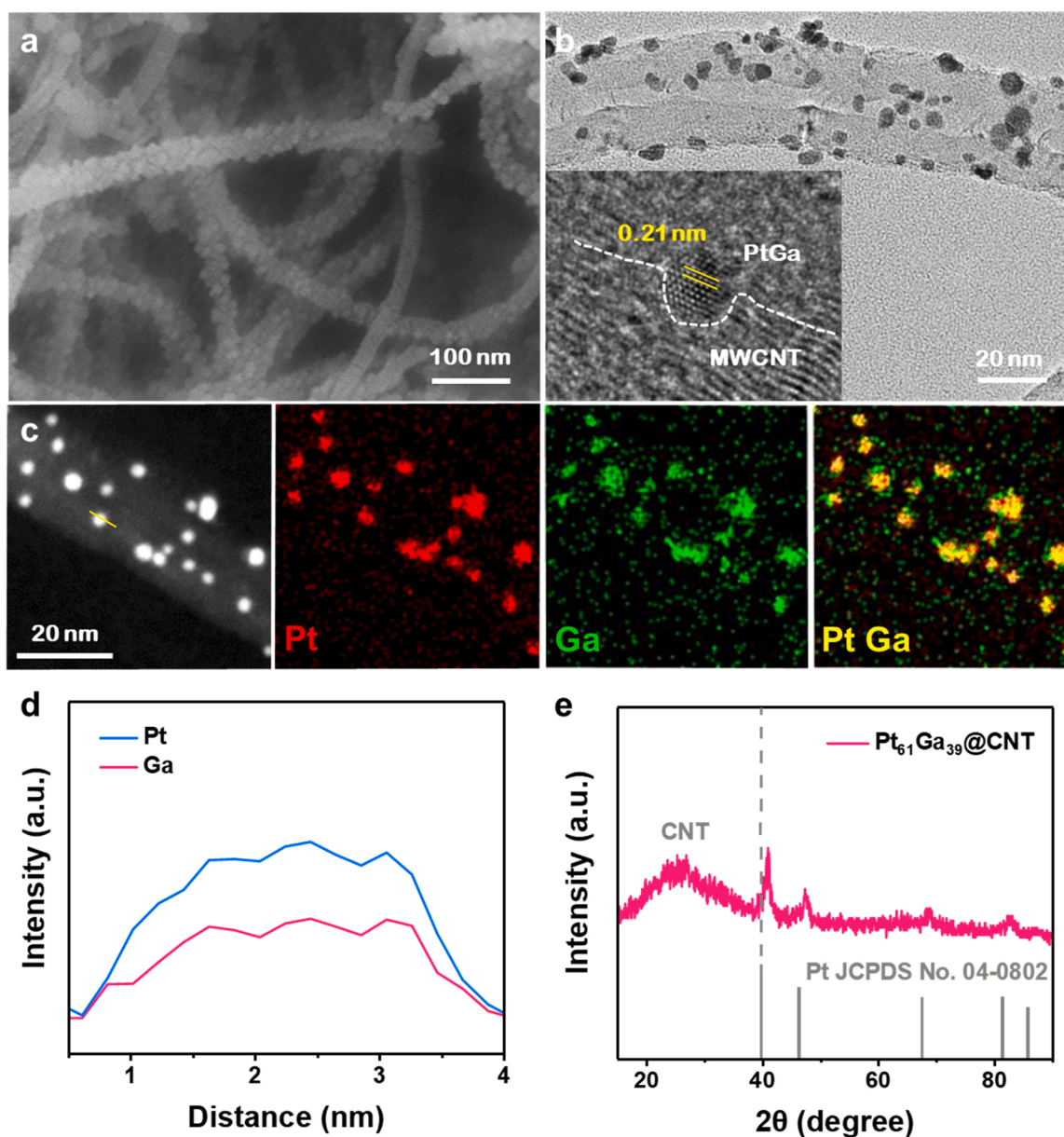


Fig. 1. Characterization of $\text{Pt}_{61}\text{Ga}_{39}\text{@CNT}$. (a) SEM image. (b) TEM image (HR-TEM insert). (c) Corresponding TEM mapping. (d) Corresponding TEM line-scanning. (e) XRD pattern.

Nevertheless, these catalysts cannot be stable under harsh conditions (commercial current densities and acidic seawater environment) due to the rapid leaching of reactive transition metals [28]. P-block metals with closed d^{10} electronic configurations are more stable than 3d transition metals and can regulate the electronic structure of Pt [29–32]. In addition, SMSI can not only stabilize the electron transfer but also prevent agglomeration and etching of nanomaterials [33,34]. This inspired us that SMSI combined with Pt-p-block alloys can solve the above problems.

Here, we present a novel strategy through SMSI and Pt-p-block alloys (PtM@CNT , $M = \text{Ga, In, Pb}$ and Bi) to construct a stable electronic perturbation and achieve acidic seawater hydrogen production performance at commercial current densities for the first time. SMSI stabilizes electron transport and promotes durability. The optimized PtGa@CNT also exhibits superior hydrogen evolution reaction (HER) properties in acidic, alkalic and acidic brine electrolytes. DFT calculation deeply reveals that the electronic perturbation of Ga on Pt increases the hydrogen adsorption capacity, thereby reducing the reaction activation energy.

And the higher vacancy formation energy in PtGa@CNT leads to a better stability.

2. Methods and experimental section

2.1. Chemicals

Platinum (II) 2,4-pentanedionate ($\text{Pt}(\text{acac})_2$, 97%) was obtained from Sigma-Aldrich (Shanghai) Trading Co., Ltd. China. Gallium nitrate hydrate ($\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$), Indium nitrate hydrate ($\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$), lead nitrate hydrate ($\text{Pb}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$), Bismuth nitrate hydrate ($\text{Bi}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$), and multi-walled carbon nanotube were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Potassium hydroxide (KOH, 90%) from Aladdin. Commercial carbon supported Pt catalyst (Pt/C , 20 wt% of 3 nm-Pt nanoparticles on carbon black) was obtained from Aladdin. Nafion solution (5%) was purchased from Sigma-Aldrich. Sulfuric acid (H_2SO_4 , 95–98%), nitric acid (HNO_3 , 95–98%) and ethanol ($\text{C}_2\text{H}_5\text{O}$) were provided by Sinopharm Chemical

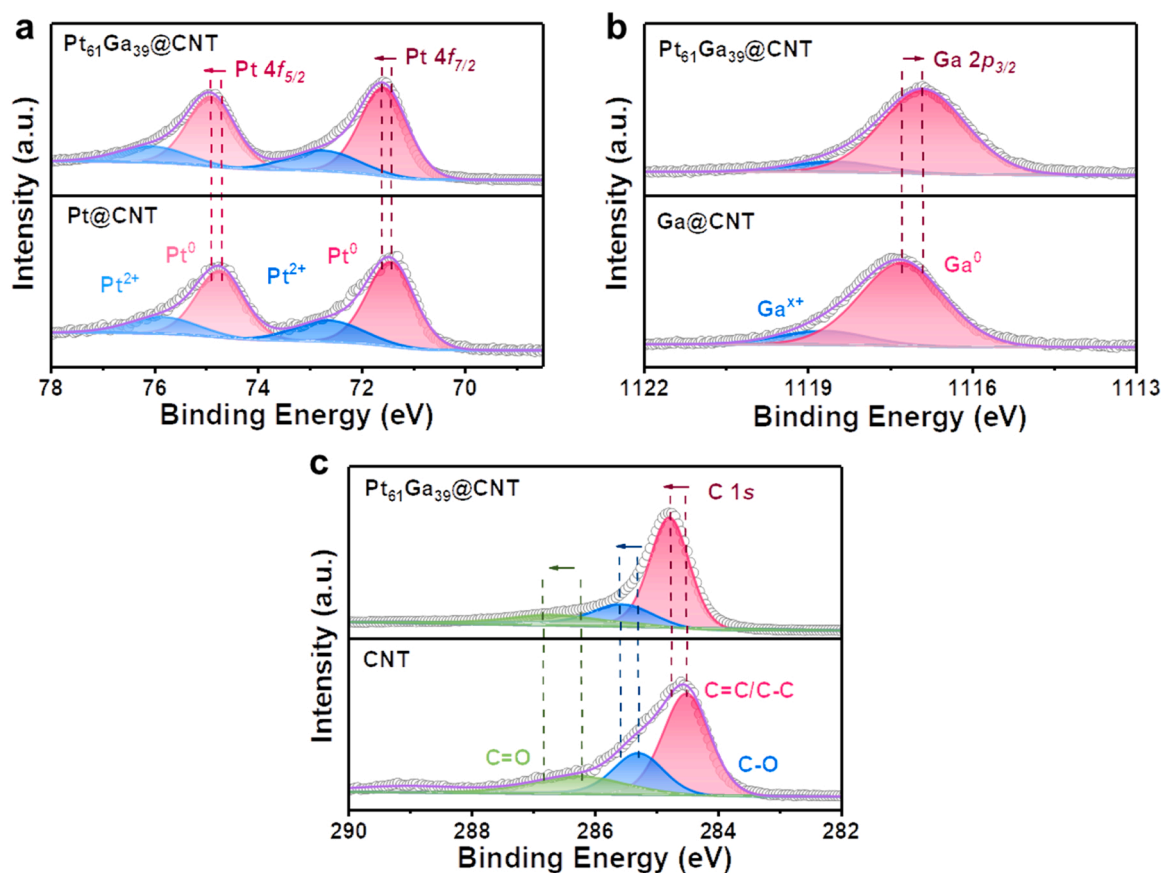


Fig. 2. XPS spectra. (a) Pt 4f of Pt₆₁Ga₃₉@CNT and Pt@CNT. (b) Ga 2p_{3/2} of Pt₆₁Ga₃₉@CNT and Ga@CNT. (c) C 1s of Pt₆₁Ga₃₉@CNT and CNT.

Reagent Co., Ltd. Ultrapure water (Millipore Milli-Q grade) with a resistivity of 18.2 MΩ was used in all the experiments.

2.2. Synthesis of PtM@CNT

All catalysts were synthesized using a solvent-free microwave method. Taking Pt₆₁Ga₃₉@CNT, for example, Pt(acac)₂ (5 mg), Ga(NO₃)₃·xH₂O (3.4 mg), and CNT (5 mg) were mixed in a mortar and ground evenly. Put the mixture into a 10 mL quartz vial, pour Ar into the bottle. Then it was placed in a household microwave oven (Midea, PM2001) and reacted for 30 s with a power of 700 W. The synthesis is initiated at room temperature and normal atmospheric pressure. The reaction mixture was then washed and centrifuged with ethanol. Finally, the product was dried overnight in a 60 °C oven to obtain a black powder.

2.3. Synthesis of Pt@CNT

The Pt@CNT was synthesized with the same procedures described above for PtM@CNT, except that there is no p-block metal salt added.

3. Results and discussions

3.1. Catalysts synthesis and physical characterizations

PtGa@CNT catalysts were synthesized by a simple solvent-free microwave reaction in a domestic microwave oven for 30 s (Fig. S1). Three samples of PtGa@CNT with different proportions (atomic ratios of Pt/Ga: 0.5, 1.5, and 2.0) were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Table S1). Among them, the PtGa@CNT catalyst with an atomic ratio of 1.5 gave the best HER

activity in 0.5 M H₂SO₄ solution (Fig. S2). We employed a scanning electron microscope (SEM) and transmission electron microscope (TEM) to study the morphology and structure of the Pt₆₁Ga₃₉@CNT. PtGa nanoparticles with very high density are grown on CNT, and feature an average size of about 3.0 nm (Fig. 1a, S3 and S4). The Pt₆₁Ga₃₉@CNT was further confirmed by the high-resolution transmission electron microscopy (HR-TEM) image (Fig. 1b). The lattice spacing for PtGa (0.21 nm) is smaller than that of Pt (111) plane (0.22 nm). This confirms that Pt and Ga are alloyed inducing a compressive strain, which might influence the electrochemical activity. Due to the instantaneous high temperature of microwave reaction, PtGa alloy is anchored on CNT with coating layer which preliminarily believed that SMSI is produced. Moreover, the elemental mapping and line-scanning acquired by energy-dispersive X-ray spectroscopy (EDS) analysis show that Pt and Ga are uniformly dispersed with an atomic ratio of 1.5, which was consistent with the ICP result (Fig. 1c-d and S5). And the weight percent of PtGa in the catalyst Pt₆₁Ga₃₉@CNT is about 18 wt%. Additionally, the X-ray diffraction (XRD) pattern (Fig. 1e) of Pt₆₁Ga₃₉@CNT shows that the characteristic diffraction peaks index well with face-centered cubic (fcc) Pt. It is worth noting that the diffraction peak of Pt₆₁Ga₃₉@CNT is slightly shifted to a higher angle region compared to the standard card of Pt, which is generated due to the lattice contraction initiated by the incorporation of Ga (122 pm) with smaller atomic radius into Pt (139 pm) [35]. The change can be attributed to the formation of a Pt-Ga alloy with a characteristic peak at 41.1°. And the wider diffraction peaks indicate a smaller dimension, further demonstrating the ultrafine properties of these catalysts [36]. The broad peak from 20° to 40° is assigned to CNT (Fig. S6). The composition and unique electronic structure were further investigated by X-ray photoelectron spectroscopy (XPS). It confirms the presence of Pt and Ga elements in Pt₆₁Ga₃₉@CNT catalyst with an atomic ratio of 1.5 (Fig. S7). As shown in Fig. 2a, Pt 4f

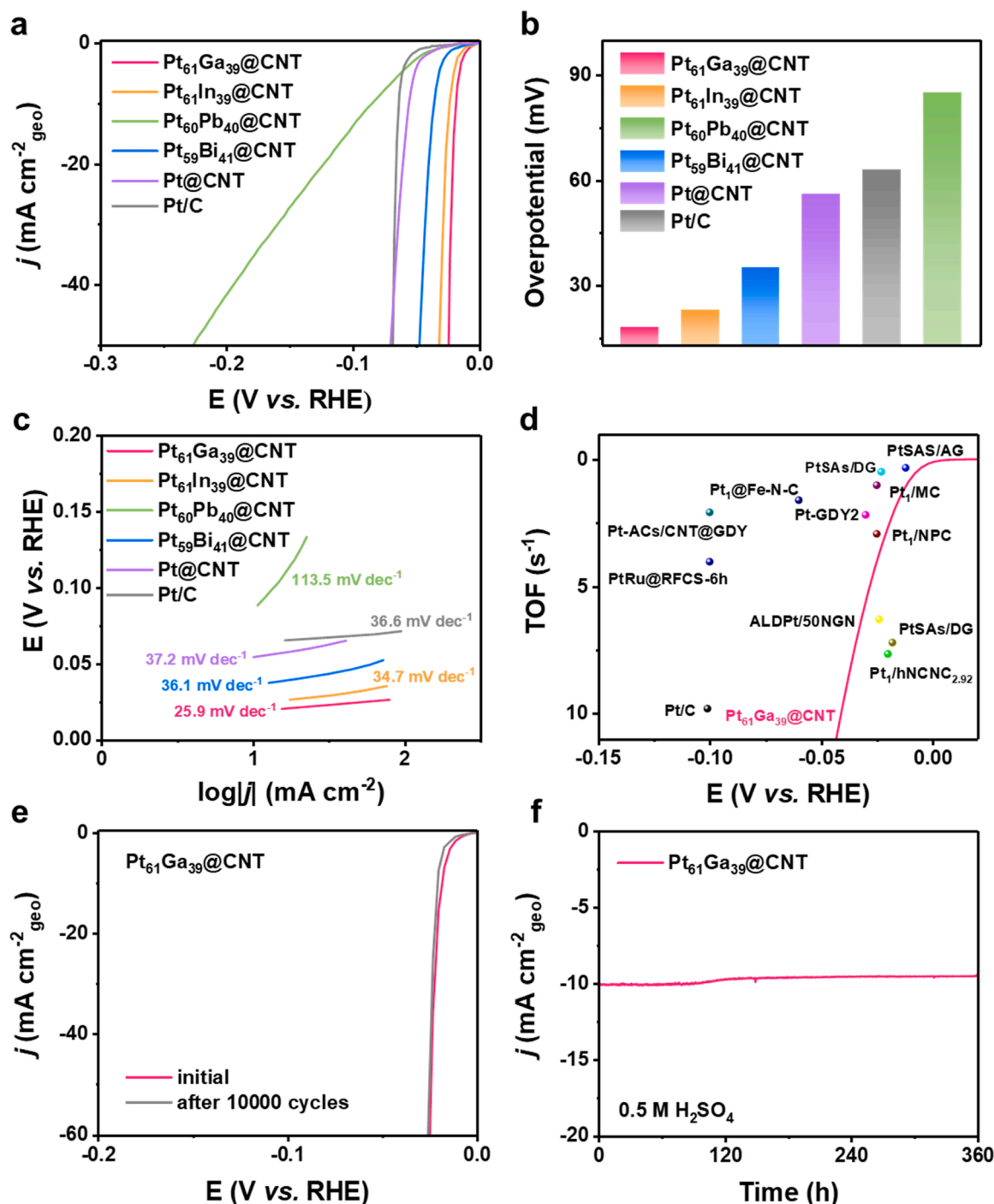


Fig. 3. Electrochemical HER performance for PtM@CNT, Pt@CNT and commercial Pt/C in 0.5 M H₂SO₄ electrolyte. (a) Polarization curves. (b) Overpotentials at 10 mA cm⁻². (c) Tafel plots. (d) TOF of Pt₆₁Ga₃₉@CNT and the comparison with the literatures. Pt/C, Pt₁/OLC [45], Pt₁/hNCNC_{2.92} [46], PtSAs/AG [47], PtSAs/DG [48], Pt-GDY₂ [49], ALDPt/50NGN [50], Pt-GT-1 [51], Pt₁/Fe-N-C [52], Pt₁/MC [53], Pt₁/NPC [54], PtSA/C-Air [19], Pt-ACs/CNT@GDY [55], PtRu@RFCS-6 h [56]. (e) Polarization curves before and after 10,000 CV cycles from 0.01 to -0.02 V vs. RHE. (f) Chronoamperometry curve at -0.018 V vs. RHE.

signal is deconvoluted into two species (Pt⁰ and Pt²⁺). The dominant metallic Pt signals for Pt₆₁Ga₃₉@CNT at 71.57 eV and 74.91 eV are obtained. Meanwhile, the two peaks at 72.73 eV and 76.05 eV correspond to Pt²⁺. Interestingly, the characteristic peaks for the Pt₆₁Ga₃₉@CNT are significantly shifted to higher binding energies than Pt. This positive shift is likely due to the introduction of Ga atoms in Pt lattice, causing the electron transformation from Pt to Ga and the valence d-band center shift [37]. Besides, the Ga 2p_{3/2} binding energies are 1116.88 eV for the zerovalent state and 1118.53 eV for the oxidized ones (Fig. 2b). The C 1 s peak of Pt₆₁Ga₃₉@CNT shifts to higher binding

energy compared to CNT, which further verified SMSI phenomenon (Fig. 2c). Solvent free microwave method can also be extended to synthesize different components of PtM@CNT (M = Ga, In, Pb and Bi) alloy catalysts. The other PtM@CNT catalysts possess similar morphology and structure by SEM, TEM, XRD, and XPS characterizations. And the surface elements ratios of Pt/M are all about 1.5 (measured by XPS). These results prove the successful formation of PtM@CNT (Fig. S8-S13). Pt@CNT is synthesized as a contrast material (Fig. S14).

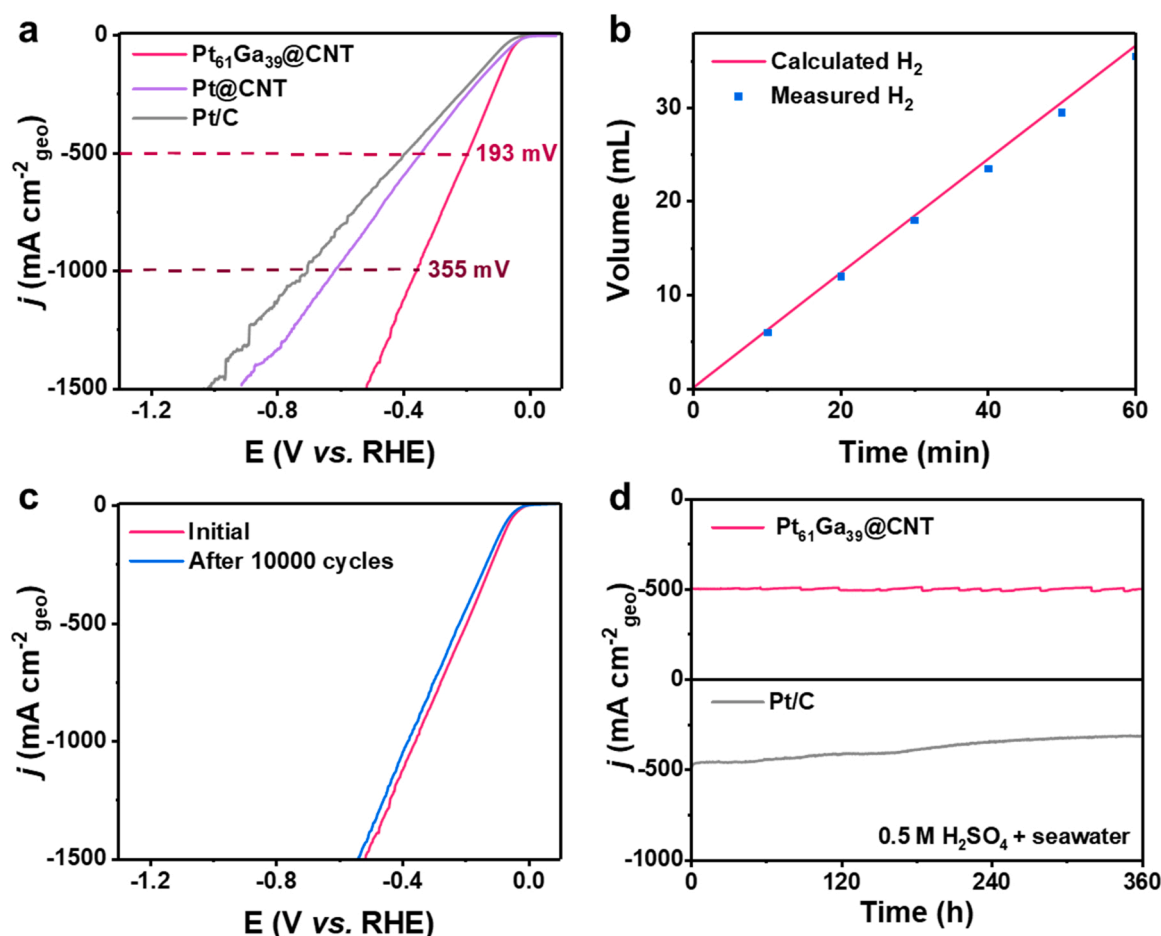


Fig. 4. Electrochemical HER performance for Pt₆₁Ga₃₉@CNT, Pt@CNT and commercial Pt/C in 0.5 M H₂SO₄ + real seawater electrolyte at high current densities. (a) Polarization curves. (b) Theoretical and experimental results of H₂ production for Pt₆₁Ga₃₉@CNT. (c) Polarization curves before and after 10,000 CV cycles from 0 to −0.15 V vs. RHE for Pt₆₁Ga₃₉@CNT. (d) Chronoamperometry curves (−0.193 V vs. RHE for Pt₆₁Ga₃₉@CNT, −0.389 V vs. RHE for Pt/C).

3.2. Electrocatalytic properties measurement

Fig. 3a shows linear scanning voltammograms (LSVs) with 95% iR in 0.5 M H₂SO₄ electrolyte, which increases in the following order: Pt₆₁Ga₃₉@CNT > Pt₆₁In₃₉@CNT > Pt₅₉Bi₄₁@CNT > Pt@CNT > commercial Pt/C (20 wt%) > Pt₆₀Pb₄₀@CNT (Fig. S15). The overpotential of Pt₆₁Ga₃₉@CNT is 18 mV at a current density of 10 mA cm^{−2}, which is 46 mV lower than commercial Pt/C (30 mV) (Fig. 3b). Pt₆₁Ga₃₉@CNT exhibits a comparable onset potential (9 mV) to commercial Pt/C (16 mV). The Tafel slope of Pt₆₁Ga₃₉@CNT (25.9 mV dec^{−1}) is minimal (Fig. 3c). And the slope derived from the steady-state polarization curve is shown in Fig. S16. This identifies a Volmer-Tafel mechanism, while the rate-determining step is the recombination of surface adsorbed hydrogen atoms. In this case, the HER proceeds through the combination of two adsorbed hydrogen atoms on Pt₆₁Ga₃₉@CNT to form molecular hydrogen. And the exchange current density (*j*₀) of Pt₆₁Ga₃₉@CNT is the highest (1.05 mA cm^{−2}). In addition, the mass activity of Pt₆₁Ga₃₉@CNT is 14.2 A mg_{Pt}^{−1} at 70 mV, which performs best compared with the other catalysts (Fig. S17). To understand the specific activities of the catalysts, the electrochemical active surface areas (ECSAs) were calculated according to the underpotential desorption of hydrogen (H-UPD) (Fig. S18). Pt₆₁Ga₃₉@CNT reaches 78.5 m²/g_{Pt} of ECSA, which is larger than commercial Pt/C (71.4 m²/g_{Pt}) (Fig. S19). Also, the ECSAs of Pt₆₁Ga₃₉@CNT measured by CO stripping (Fig. S20) and underpotentially deposited of Cu (Cu-UPD) (Fig. S21) experiments are 86.4 m²/g_{Pt} and 98.3 m²/g_{Pt} respectively. The number of active sites (*n*)

calculated by Cu-UPD of Pt₆₁Ga₃₉@CNT is 2.1 × 10^{−3} mol/g_{Pt}, which is higher than commercial Pt/C (1.6 × 10^{−3} mol/g_{Pt}) [38]. Moreover, Pt₆₁Ga₃₉@CNT displays an advantageous specific activity of 81.6 mA cm^{−2} at 70 mV (normalized by H-UPD) (Fig. S22). The TOF value of Pt₆₁Ga₃₉@CNT reaches 37.34 s^{−1} at 100 mV, which can outperform the most reported catalysts (Fig. 3d and S23). Electrochemical double-layer capacitance (*C*_{dl}) calculated by CV tests at different scan rates are shown in Fig. S24. Next, the H₂ produced during the reaction was collected and tested by gas chromatography, and the Faraday efficiency is close to 100% (Fig. S25). A detailed comparison of Pt-based HER catalysts in 0.5 M H₂SO₄ electrolyte is listed in Table S2. The 10,000 cyclic voltammetry (CV) cycles (Fig. 3e) and chronoamperometry (Fig. 3f) measurements observe that Pt₆₁Ga₃₉@CNT demonstrates a high degree of durability in an acidic medium. After the stability test, we conducted SEM, TEM, XRD, and XPS characterizations of the electrocatalyst (Figs. S26 and S27), and found that the morphological feature and structure are basically maintained. Additionally, there is a minor leaching of Ga from the surface of the catalyst after long-term HER stability test (Table S3).

Further, we test the HER performance of PtM@CNT (M = Ga, In, Pb and Bi) in 1.0 M KOH electrolyte. Pt₆₁Ga₃₉@CNT reaches the smallest overpotential (20 mV at 10 mA cm^{−2}), Tafel slope (31.7 mV dec^{−1}) and the TOF of 21.33 s^{−1} at 100 mV (Figs. S28 and S29). At the same time, Pt₆₁Ga₃₉@CNT shows satisfactory mass activity (Fig. S30) and specific activity (Fig. S31). *C*_{dl} value is the highest (Fig. S32). And the Faraday efficiency is close to 100% (Fig. S33). Excellent stability is also found in 1.0 M KOH (Fig. S34).

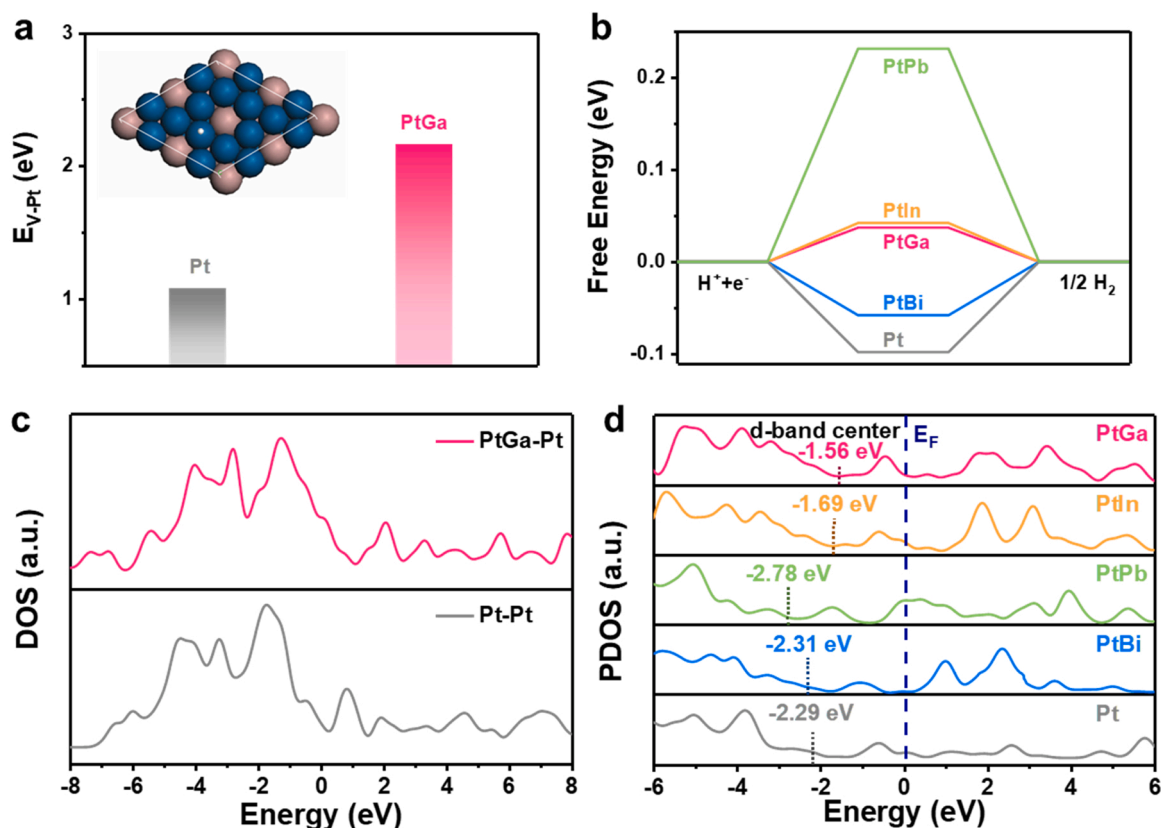


Fig. 5. DFT calculation. (a) E_{v-Pt} for Pt and PtGa, and the inset shows the crystal structure. The blue, pink and white spheres represent Pt, Ga and H atoms respectively. (b) Free-energy barriers of different catalysts. (c) DOS of Pt atoms for PtGa and Pt. (d) Calculated PDOS of different catalysts with d-band center positions.

The average salinity of seawater is about 0.599 M, mainly NaCl. Continuous electrolysis process will accumulate chloride and accelerate electrode corrosion. As shown in Fig. S35a, Pt₆₁Ga₃₉@CNT exhibits the best HER activity in 0.5 M H₂SO₄ + 0.6 M NaCl. The overpotential of 25 mV is needed to drive a current density of 10 mA cm⁻² (Fig. S35b). The Tafel slope of Pt₆₁Ga₃₉@CNT is 25.6 mV dec⁻¹ (Fig. S35c). Besides, Pt₆₁Ga₃₉@CNT performs a decent mass activity (Figs. S36). To explore the catalytic performance in large-scale industrial production, Pt₆₁Ga₃₉@CNT was dripped on a carbon cloth to obtain accurate high current density. It exhibits well in whether the acidic simulated seawater (Fig. S37) or the acidic natural seawater (Fig. 4). Pt₆₁Ga₃₉@CNT only needs 193 mV and 355 mV to reach the current density of 500 and 1000 mA cm⁻² in 0.5 M H₂SO₄ + real seawater electrolyte (Fig. 4a). The gas amounts match well with the calculated results, indicating a nearly 100% Faradaic efficiency (Fig. 4b). Polarization curves of Pt₆₁Ga₃₉@CNT show negligible shift relative to the initial state after 10,000 cycles (Fig. 4c). It can function for more than 360 h to maintain a current density of 500 mA cm⁻² which is more stable than commercial Pt/C (Fig. 4d). The surface morphology and crystal structure of the electrode are well maintained after the stability test (Figs. S38 and S39). In the two-electrode system, Pt₆₁Ga₃₉@CNT||RuO₂/C was prepared by loading Pt₆₁Ga₃₉@CNT and commercial RuO₂/C on carbon cloth as the cathode and anode. It can be seen in Fig. S40 that the Pt₆₁Ga₃₉@CNT has a better overall seawater splitting performance than commercial Pt/C, which can reach 500 mA cm⁻² at 2.72 V.

3.3. DFT technique

DFT calculation is carried out to understand the HER reaction mechanism in acidic simulated seawater at atomistic insight. The theoretical models are constructed for PtM (M=Ga, In, Pb and Bi) based

on the corresponding structural and compositional parameters (Fig. 5a, inset). As shown in Fig. 5a, PtGa has a higher vacancy formation energy for a Pt atom (E_{v-Pt}). It suggests that the incorporation of Ga atoms increased the E_{v-Pt} , confirming the improved structural stability of PtGa@CNT. Fig. 5b shows the ΔG_{H^*} of different alloy materials, and PtGa has the Gibbs free energy closest to zero (0.037 eV). It shows that PtGa alloy is conducive to the adsorption and desorption of H, consistent with the experimental results of HER performance. As shown in Fig. 5c, the density of states (DOS) plots demonstrate that there are some new hybrid electronic states in PtGa alloy compared to pure Pt. It may be caused by the atomic hybridization between Pt and Ga [39]. And the electron-occupied state near Fermi level on PtGa is much higher than Pt, giving evidence of a stronger carrier density which is conducive to improving the hydrogen adsorption capacity [40]. This is reasonable to the obvious electron transfer in the XPS analysis results [41]. The partial densities of states (PDOS) results are shown in Fig. 5d. Compared with PtGa (-1.56 eV), d-band centers of PtIn (-1.69 eV), Pt (-2.29 eV), PtBi (-2.31 eV) and PtPb (-2.78 eV) shift farther to the Fermi level. The d-band center of the electrocatalyst has a linear relationship with the hydrogen binding energy. The higher d-band center, the stronger hydrogen binding energy of reaction intermediate on the catalyst surface (H^* adsorption) [42,43]. Due to the electrons transfer from Pt to Ga and In elements, the d-band centers of PtGa and PtIn shifted positively compared with pure Pt. It indicates that the introduction of Ga or In enhances H^* adsorption and promotes the Volmer step. On the contrary, the d-band center shift of PtPb is significantly negative than Pt, which means a weaker H^* adsorption and inhibits the catalytic activity. And the d-band center of PtBi is similar to Pt, showing that the addition of Bi has no great influence on the H^* adsorption capacity of Pt. Overall, the d-band centers of PtM have different degrees of deviation than that of Pt, indicating the electronic disturbance of p-block metals to pure Pt,

resulting in the p-d hybrid orbital [44]. Therefore, the optimized electronic structure of PtGa is more conducive to high catalytic activity.

4. Conclusion

In summary, we present a novel strategy through SMSI and Pt-p-block alloys (PtM@CNT, M = Ga, In, Pb, and Bi) to construct a stable electronic perturbation and achieve acidic seawater hydrogen evolution performance at commercial current densities for the first time. SMSI stabilizes electronic perturbation and improves the catalytic durability up to 360 h. The optimized Pt₆₁Ga₃₉@CNT requires a quite small overpotential of 18 mV to deliver a current density of 10 mA cm⁻² in 0.5 M H₂SO₄ and first achieves a low overpotential of 193 mV and 360 h stability at 500 mA cm⁻² in acidic seawater. DFT calculation reveals that PtGa has excellent ΔG_{H*} (0.037 eV) and the closest d-band center of Pt to Fermi level. The good stability of PtGa@CNT originates from the higher vacancy formation energy. Overall, this discovery not only first achieves stable acidic seawater hydrogen production under commercial current densities, but also opens a new opportunity to explore catalytic applications of p-block alloys and SMSI stabilized electronic perturbation.

CRediT authorship contribution statement

Nanzhu Nie: Investigation, Data curation, Conceptualization, Formal analysis, Validation, Writing – original draft. **Dan Zhang:** Validation. **Zuochao Wang:** Investigation. **Shijie Ge:** Formal analysis. **Yanli Gu:** Formal analysis. **Bo Yang:** Supervision. **Jianping Lai:** Conceptualization, Writing – review, Supervision, Funding acquisition. **Lei Wang:** Funding acquisition, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (51772162, 22001143, and 52072197), Youth Innovation and Technology Foundation of Shandong Higher Education Institutions, China (2019KJC004), Outstanding Youth Foundation of Shandong Province, China (ZR2019JQ14), Taishan Scholar Young Talent Program (tsqn201909114, tsqn201909123), Natural Science Foundation of Shandong Province (ZR2020YQ34), Major Scientific and Technological Innovation Project (2019JZZY020405), and Major Basic Research Program of Natural Science Foundation of Shandong Province under Grant (ZR2020ZD09).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2022.122100](https://doi.org/10.1016/j.apcatb.2022.122100).

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